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Method for making paper, assembly for implementing the method and paper product produced by the method

5 The invention relates to method according to the preamble of claim 1 for manufacturing coated paper, board or similar product having a plant fiber base, in which method a layer of coating furnish is applied and adhered to a base web made of the fibers. The coating furnish at least partially consists of a carbonate compound.

The invention also relates to an assembly suitable for implementing said method and a plant-fiber-based product coated with said carbonate-based coating furnish.

15 In the context of the present application, the term paper is used when reference is made to any product produced on a plant fiber base such as a web of paper or board.

20 Generally, webs of paper and board are coated in order to enhance their printability properties. Among other things, the purpose of the coating is to improve the smoothness and whiteness of the base web and, particularly with thin base webs, to increase the opacity of the web material. Conventionally, the coating is applied to the base web surface as an aqueous suspension. There may be applied a plurality of coat layers and the application of the coat layers can be accomplished using a number of different methods. Since all the conventional methods 25 apply the coating as an aqueous suspension, the drying of the coat forms a massive step in the coating process. Drying of the coat is an energy-intensive process and the drying of a fast moving web needs a long dryer section in order to direct a sufficient amount of drying energy to 30 the web. Also the routing of the web to be processed is difficult; because the web cannot be guided by any members contacting it from its wet side until the coating 35

has become adequately dry.

It is an object of the present invention to overcome the disadvantages of the above-described technology and to 5 provide an entirely novel type of application method for coating a paper web.

The goal of the invention is achieved by forming the coating from microparticulate calcium carbonate or precursors thereof, said microparticulate coating being 10 transferred to the web in dry form or as a suspension of 15 a high solids content.

More specifically, the method according to the invention 15 is characterized by what is stated in the characterizing part of claim 1.

Further, the assembly according to the invention is 20 characterized by what is stated in the characterizing part of claim 38.

Still further, the paper web product according to the invention is characterized by what is stated in the characterizing part of claim 55.

25

The invention offers significant benefits.

By virtue of the invention, a web can be coated without 30 using any water in the coating furnish, whereby also the web need not be dried during any step of the coating process and no equipment is required for preparing an aqueous coating mix. The overall length of the coater can be made shorter and its construction may be simplified. Because a major fraction of the energy consumed at the 35 coater is used for drying the aqueous coating suspension, the invention offers significant savings in the specific energy consumption of coated paper grades. The invention

may be combined with a dry base web-formation method (cf. FI Pat. Appl. No. 973775 filed by the applicant), thus permitting the entire papermaking process to be carried out without any drying steps or, alternatively, using a minimal amount of water and drying. During web formation, calcium carbonate or its precursors can be fed into the fiber mass, whereby also the filler is introduced into the web. As known, calcium carbonate particles or the formation thereof in the web improves the interfiber bonding, whereby the web becomes stronger than a web containing no fillers.

By virtue of the invention, the paper surface can be provided with a coat of superior hiding power and smoothness. This kind of paper offers excellent printability. Moreover, coat defects such as streaking, orange peel patterning, uncoated patches and the like typically occurring in conjunction with blade, film-transfer and other known coating methods are eliminated. The dust of coating material can be effectively adhered to the web, whereby the soiling of the operating environment and equipment is smaller than with conventional wet coating methods. The method can be combined with known coating methods, thus permitting a dry coating to be applied on a wet coat and vice versa. The method can cost-effectively produce thick coats, because there is no need for intermediate drying between the application of successive coat layers and the thickness of a coat layer is limited only by the adherence of the coating to the web surface. To obtain heavy coat weights, it may be necessary to use binders that are applied to the web simultaneously with the coating or, during a separate step, under or over the coat. The calcium carbonate particles can be prepared in a separate process or coating equipment, or even directly onto the web.

In the following the invention will be examined in

greater detail with the help of exemplifying embodiments illustrated in the appended drawings in which

Figure 1 shows a first embodiment according to the
invention;

Figure 2 shows a second embodiment according to the
invention;

Figure 3 shows a third embodiment according to the
invention;

Figure 4 shows a fourth embodiment according to the
invention;

Figure 5 shows a fifth embodiment according to the
invention;

Figure 6 shows a sixth embodiment according to the
invention;

Figure 7 shows a seventh embodiment according to the
invention; and

Figure 8 shows an eighth embodiment according to the
invention.

Int. Pat. publication WO/96/237228 and FI Pat. Appl. 964,365 describe a method for preparing extremely small and homogeneously sized PCC (Precipitated Calcium Carbonate) particles. In this method, PCC particles are formed from slaked lime CaO with the help of water and carbon dioxide in a direct gas-phase reaction, whereby extremely small particles are created with a diameter smaller than 100 nm, even smaller than 20 nm. There is also described a method for coating particles of natural calcium carbonate with precipitated carbonate. Under

suitable conditions, the prepared elementary particles floc into roundish aggregate particles of a cloudberry shape that have better rheological and optical properties than conventional PCC particles of needle-like shape. The
5 size distribution of the flocced aggregate particles is very narrow and the flocced particles made using this technique are almost invariably smaller than 500 nm. The particles forming the aggregates are bonded to each other by van der Waals and capillary forces that become
10 effective when the particles are disposed from each other at a distance smaller than 100 nm. On the other hand, the zeta-potential that characterizes the potential difference of the particle's ion field to the medium tends to separate the particles from agglomerating with
15 each other. As the zeta-potential is strongly dependent on the pH of the particle, the formation and size of the aggregate particles can be affected by varying the degree of turbulence, or average mutual distance, and pH of the particles tending to aggregate together. If the degree of
20 turbulence in the particle flow is sufficiently high, the elementary particles can be kept apart from each other. A more detailed description is given in cited patent applications.

25 In the most advantageous embodiment of the invention, the use of PCC made using the novel technique is combined with application to a web by means of ion-blasting. Thus, when PCC is transferred, e.g., by ion-blasting to the web surface, the particles are bonded directly to each other
30 and the web surface by van der Waals and other forces even without using any additional binder. Resultingly, the web is coated with a homogeneous and hiding layer of carbonate particles that has the same toughness as the single carbonate aggregates even though it smoothly
35 covers the entire web of fibers. Coat application may also be accomplished using a gas flow, whereby a flow is directed tangential to the web surface performs so as to

smooth away the irregularities of the web surface when the particulate matter coating accumulates in the depressed points of the web in the same manner as drifting snow. The carbonate particles may also be impinged with a high velocity perpendicular to the web, whereby the carbonate particles are penetrated into the interstitial spaces between the web fibers thus introducing a filler into the base web. By virtue of this technique, the web-formation section of a paper machine can be constructed without a filler feed system.

Slaked lime and/or calcium hydroxide can be transferred to the web surface, e.g., at the press section of the paper machine by gas flow or, alternatively, by ion-blasting. Subsequently, the calcium oxide is let to react with water fog, liquid water or steam to form calcium hydroxide, after which the web is taken to a carbon dioxide atmosphere and there the reaction is continued forming calcium carbonate on the web surface, wherein the carbonate particles thus formed adhere to the web. When the method is combined with dry formation of the base web, the calcium oxide or calcium hydroxide can be introduced as one constituent of the web and then reacted into calcium carbonate. Herein, the web dry-forming step can be performed so that into the formed web of fibers are introduced nano-size particles of calcium carbonate that in the mix of fibers bond the fibers and particles into a strong web. Thus, it is possible to form a web entirely from a dry furnish and, furthermore, to replace a fraction of the fibrous raw material with calcium carbonate, whereby the amount of fibrous raw material can be reduced to a minimum from that customarily required in a finished web.

An important feature of the invention is the possibility of recycling the calcium carbonate of deinked waste paper by feeding the precipitated calcium carbonate of the

deinking process to a calcination plant. The calcium oxide obtained from the calcination plant can be treated into precipitated calcium carbonate that may then be used in the manner described cited publications and the
5 present application.

The present application utilizes the so-called ion-blast technique. This technique is based on forming a strong electric field, between one or typically a plurality of
10 pointed electrodes and one planar counterelectrode. The tip of the pointed electrode emits a corona discharge that charges particles located in the vicinity of the electrode tip thus causing the generation of ions in the electronegative gaseous medium. The ions migrate along
15 the field lines extending between the electrode and the counterelectrode which is taken to the ground potential or to a lower potential, whereby the ions adhere to particles they meet on their travel. The electric field transports the charged particles over the interelectrode
20 gap toward the ground-potential electrode, where they attach to the substrate by electric and mechanical forces. If the distance between the opposed electrodes is large and the applied voltage is high (more than 50 kV),
25 a gas flow is established between the opposed electrodes that mechanically transports the charged particles toward the ground potential. This flow is conventionally known as ion blast. In the ion-blast phenomenon, the electric field exiting from the tip of the electrode forms a conical field pattern in which the ionized gas and
30 charged particles move. Ion blast can transport both solid particles and liquid droplets.

In papermaking, the ion-blast technique can be utilized for binding a raw material to a web-formation substrate or for transferring and adhering the coating to the surface of a paper or board web. Basically, the substrate
35 can be any surface permittive to the electric field or,

alternatively, an electrically conducting surface. As the web in a continuous process must be formed on a moving surface, the web-formation substrate conventionally is a wire, felt or belt. In principle, the smoother the surface can be on which the web is formed. In coat application, the formation substrate is the surface of a paper or board web.

In Fig. 1 is shown one embodiment of the invention. The calcium carbonate particles are here formed directly in a gas phase in a chamber 1 as described in above-cited patent applications and are taken therefrom via a tube 2 into a particle circulation path 3 formed by a circular tube. In the particle circulation, there is maintained a continuous flow (denoted by arrow 4) serving to keep the particles in a continuous motion and preventing their floccing into excessive large aggregates. Additionally, floccing can be controlled by altering the pH of the particulate matter fed into the circulation, whereby the zeta-potential of the particles is lowered and the floccing tendency is reduced. Correspondingly, the aggregate size can be increased by elevating the pH level of the particles. The particle circulation tube 3 is passed to an ion-blast zone 6 formed into a chamber 21. Via the chamber 21 is also passed a paper or board web 11 to be coated, as well as a conducting wire 15 supporting the same. In Fig. 1, the web is shown travelling from the left to the right. The wire 15 passes over guide rolls 12, 13, 14 so as to form an endless loop. The wire 15 is grounded or taken to a low potential via a connection 16 made to a guide roll 14, for instance.

To the interior of the ion-blast chamber 21 and directed toward the web 11 and the wire 15, there are adapted a plurality of pointed-tip electrodes 22 connected via a conductor 5 to a power supply 23. From the power supply, a high potential relative to the conducting wire 15 is

applied to the electrodes 22, whereby between the electrodes and the wire is created an ion-blast zone 7 of conical flux tubes of the electrical field that directs the particulate matter flow toward the web 11. As the
5 field lines leaving the tip of each pointed electrode 22 form a flux tube of a conical shape, the number and location of electrode tips must be configured so that the conical flux tubes leaving the staggered electrode tips provide a uniform field on the surface of the web 11. The
10 applied electrode voltage is dependent on the distance between the counterelectrode formed by the conducting wire 15 and electrode tips 22 that may be varied from 2 mm to 2 m; however, to keep the space requirements of the coating furnish feed equipment within practicable
15 limits, an interelectrode distance range of 100 - 1000 mm is favoured. While a large interelectrode distance as such does not impair the function of the apparatus, it increases the external dimensions of the system and complicates the behaved control of material flows in the
20 chamber 16. When using a design based on the practicably most favourable interelectrode distance range, the voltage applied between the opposed electrodes is typically set in the range 80 - 160 kV, but may be varied as widely as from 30 kV to 1000 kV. The counterelectrode may be run
25 positive or negative, and the electrode tips may respectively be connected to the negative or positive terminal of the power supply.

As the particle flow fluidized by the carrier gas is continuously circulated via the chamber 21, the direction of the particle flow is affected by the velocity vector of the circulation and, hence, the direction of the particle path is incident on the web in the reverse direction to the travel of the web 11 as indicated by arrow 8 in the
30 diagram. When the particles hit the surface of the web 11, they are brought to a close distance from each
35 other and the fibers of the web, whereby they become

attached to the fibers and each other due to van der Waals and other forces, thus forming a tight and uniform layer of coating. Furthermore, the particle flow which is blasted obliquely against the travel of the web surface 5 accumulates calcium carbonate particles in the depressed points of the web surface, whereby the profile of the coated surface becomes smoother. The adhering capability of the particles can be further improved by treating the web 11 with water or chemicals sprayed thereon prior to 10 its entry in the ion-blast chamber. As known, water establishes hydrogen bonds between the fibers of the paper web and also improves the bonding of the calcium carbonate particles to the fibers and to each other. The 15 coated web 11 may be further treated by a binding agent, water or chemicals sprayed from nozzles 10 located after the ion-blast chamber 21. It must be noted that the amount of water used in the method according to the invention is very minimal as compared with methods based on applying the coating as an aqueous suspension to the web. 20 Hence, the need for high-capacity dryers is eliminated.

The ion-blast apparatus may under some conditions act as 25 a capacitor that accumulates an electric charge, whereby the forces adhering the web to the conducting wire become unwieldy after the web has exited from under the counter-electrode. To discharge such adhering forces, a positive- or negative-potential corona discharge treatment 18 shown 30 in Fig. 2 can be applied downstream from the web-formation section. Instead of having a pointed tip, the electrodes 22 of the ion-blast apparatus may be planar or rail electrodes, and respectively, the counterelectrode need not necessarily be taken to the ground potential 35 with the provision that its potential must obviously be lower than that of the corona-discharge-emitting electrodes. Also the ion-blast chamber 21 may be preceded by a corona discharge device 17 serving to bring the web surface to a suitable potential and to adhere the web to

the conducting wire at the meeting point of the web with the wire.

The bonding strength of the coating to the web fibers may also be enhanced by a mechanical or thermal treatment or a combination thereof as shown in Fig. 3. In this configuration, on the travel of the web after the ion-blast chamber 21 there is arranged a pair of rolls 19 having the web 11 being treated passing through the compressive nip between the rolls. Since the web is practically dry, it can be passed directly into the nip of the compressive rolls. The rolls 19 may be, e.g., of the same type as the rolls used in calenders and the web finishing treatment can be performed using force levels equivalent to those used in calendering, thus permitting the finished web surface to receive gloss simultaneously with gaining an improved adherence of the coat. In conjunction with a surface treatment similar to calendering, it is advantageous to control the web moisture content to a proper level by means of water or mist ejected from nozzles 9. The web may be treated with water spraying or steam injection also before it passes over the rolls. In the embodiment shown in Fig. 4, the adherence of the coating is enhanced by means of electromagnetic radiation. The radiation emitter is denoted by reference numeral 20 and the type of radiation applied may be infrared, ultraviolet, radioactive or x-ray radiation or microwave energy. A particularly advantageous technique is to combine the application of radiation with web treatment by a chemical responsive to the radiation used. Such treatment chemicals can be applied to the web in the above-described manner either in front of or after the ion-blast chamber. In Fig. 5 is shown a simplified embodiment of the invention, in which the nano-size coating particles are adhered to the web and each other by van der Waals forces alone without using any other treatments.

In Fig. 6 is shown a method and apparatus for forming a carbonate coating layer directly from precursors on the surface of the web 11. In this method, the ion-blast chamber 21 with its coating particle circulation and the structure of the conducting support belt are similar to those of the above-described apparatuses. The difference herein is that the particle circulation in the present case is fed with slaked slime particles CaO that are transferred to the web surface by ion-blasting. Next, the web is passed into an enclosure 24 where water is applied to the web, e.g., under a steam or mist atmosphere. Alternatively, the water may be introduced as mist or steam in the ion-blast chamber 21 or using any other suitable technique. When the slaked lime CaO reacts with the applied water, calcium hydroxide $\text{Ca}(\text{OH})_2$ is formed. Next, the web 11 is passed into a chamber enclosing a carbon dioxide atmosphere partially or purely comprised of carbon dioxide, whereby the calcium hydroxide $\text{Ca}(\text{OH})_2$ reacts with the carbon dioxide so as to form calcium carbonate particles on the web surface. The water released in the reaction is discharged from the chamber. When desired, the adherence of the formed particles to the web surface may be secured by ion-blasting, whereby also a blast of carbon dioxide gas can be directed to the web surface.

Alternatively, a blast of powdered calcium hydroxide may be directed to the web surface, whereby the reaction described above is effected under a carbon dioxide atmosphere. Again, the applied powdered material and the carbon dioxide gas can be directed to the web and adhered thereto by means of ion-blasting. Further alternatively, the calcium hydroxide may be introduced to the web surface as an aqueous solution by spraying from jet nozzles, whereby the required carbon dioxide can be blown along with the atomizing air of the jet nozzles via orifices

made to the jet nozzles. In the latter case, the reaction forming the calcium carbonate occurs partially airborne and partially on the web surface. When using particulate PCC, the agglomeration of the formed particles can be
5 impeded by introducing external energy in the manner described, e.g., in conjunction with the discussion above related to Fig. 4. To enhance the adherence of the particles, the surface charge states of the paper web fibers may be altered by various physical or chemical
10 treatments using, e.g., alum, polymer, electrolytic or corona discharge treatments and altering the pH level of the process. The coating structures thus formed may be processed further using the above-mentioned types of treatments and mechanical treatments such as calendering.

15

In addition to those described above, the present invention may have alternative embodiments.

The coating material consisting of nano-size PCC that was
20 used in dry-coating tests is formed in a gas phase without a slurring step in an aqueous medium. The native particles are in amorphous form and their crystallization takes at least some seconds or minutes. In its amorphous form, the workability of the material is much better than
25 that of a crystalline material. However, after some time the material undergoes crystallization and the workability of the material decreases which means that its stiffness increases. This phenomenon may be utilized in the surface treatment of a paper or board web. In tests performed,
30 it has been found that the nano-size PCC is not in crystallized form directly after the coating process, but after some time the crystallization of the particles can be seen as scattering points under a microscope.

35 In its amorphous form, that is, immediately after the carbonization of calcium hydroxide, the applied coating is readily workable. Hence, the nano-size PCC should be

calendered or otherwise smoothed immediately after the application. Then, the calendering effect is imposed on the readily workable amorphous, cloudberry-like calcium carbonate aggregates (nano-size PCC). The aggregates are durable under the plastic deformation and can be levelled under the calendering pressure to form a smooth surface. Also the individual aggregates undergo a plastic deformation. Resultingly, a surface with an extremely smooth and level profile is obtained. The levelling of the web surface to a smooth profile immediately after application may be implemented using the following techniques:

5 a) cold calendering involving mechanical compaction, whereby the fixation of the aggregate particles may also require the use of a specific binding agent if the bonding forces between the fibers of the base web and the coating particles are not sufficiently strong to ensure so strong bonds that the coating material can adhere in a secure manner to the web surface;

10 b) hot calendering in which the water contained in the aggregate particles is released during hot calendering under the hot calender roll thus improving the formation of hydrogen bonds between the aggregate particles of the coating material (this does not exclude the use of bond-formation-promoting additives) and the paper web, as well

15 as the formation of interparticle bonds. The test results of this latter technique have been positive.

In Fig. 7 is shown a further embodiment of the invention suited for exploiting the above-described phenomenon.

30 Herein, the coating is applied to the web 11 by means of an applicator 26 using any of the above-described techniques. Next after the applicator 26 is placed a calender in which the roll 27 facing the coated side of the web or the roll 28 facing the uncoated side of the web or even

35 both rolls are hot rolls. In addition to the hot rolls, steam or treatment chemicals may be applied to the web, before or after the coat application. Calendering is

carried out immediately after application while the PCC
is still in its amorphous state. As mentioned above, the
coating material particles are amorphous when leaving the
carbonization process. The coat application step may be
5 complemented with binding agents, polymers,
advantageously resins, latexes or natural binding agents
that enhance the forces adhering the coating material
particles to the paper web and bind the particles to each
other. PCC aggregates are durable under the plastic
10 deformation and can assume a smooth surface structure
under the contact pressure of calendering. Also the
individual aggregate particles are deformed. To avoid
crystallization prior to calendering, the delay time from
coat application to calendering must be sufficiently
15 short. Since this delay time t is dependent on the
properties of the PCC used, the web travel distance from
the applicator to the calender is advantageously made
adjustable so that the instant of calendering with regard
to the progress of crystallization can be controlled.
20 Under normal operating conditions, however, the time of
crystallization is so long that the calendering must
invariably be carried out while the coating is still in
its clearly amorphous state.

25 In dry-coating tests performed, the paper web has been
subjected to abrasion with a mechanical brush that
fibrillates the web surface thus improving the adherence
of coating material particles to the surface structure of
the fiber matrix. The principle of the fibrillation
30 handling is shown in Fig. 8. In this technique, the sur-
face of the web 11 is abrasively treated with a brush 29
made from a suitable material, whereby microfibrils 30
are elevated from the fibers of the web. As known,
rubbing of two dielectric materials against each other,
35 e.g., by brushing movements creates static electricity.
In this manner, charging of a dry paper web with static
electricity is relatively easy. Since dry paper falls

midway on the scale of dielectric materials by its tribo-electric properties, suitable brush materials are readily available for charging a paper web with positive or negative static electricity. This technique may be applied to alter the properties of a paper web surface, e.g., for a subsequent ion-blast treatment.

Web surface fibrillation by brushing improves the adhesion of coating material particles by:

- 10 a) increasing the specific surface area (through fibrillation)
- b) increasing the coarseness of the web surface
- c) generating static electricity.

15 During brushing, the surface of a paper web to be dry-coated is fibrillated in brushing pretreatment step (by separating the fibrils of the walls of the most superficial fibers of the fibrous web matrix so much that their one end remains attached to the basic fiber while 20 the other end of the fibril remains hanging free).

The degree of surface-fibrillation can be controlled by altering the rotational speed of the brush and using different brushing pressures. The brush may be rotated 25 along or reverse to the web travel. The paper web surface can be charged with static electricity by selecting the brush material so that a desired polarity, that is, positive or negative charge, is generated on the web surface. Analogously, the amount of static electricity 30 generated herein can be controlled by altering the rotational speed of the brush and using different brushing pressures. Also analogously, the brush may be rotated along or reverse to the web travel.

35 While the use of calcium carbonate aggregate particles alone for treating a moving web is described in the foregoing examples, also other types of pigment particles may

be used such as silicates, plastic pigments titan oxide and other mineral based pigments. However, the particle size under all conditions must be so small that the interparticle and particle-to-web adherence can be accomplished by van der Waals forces, possibly augmented with ion and hydrogen bonds serving to bond the fibers together with each other. The average size of the pigment particles should be in the range of 0.5 - 100 nm, advantageously 15 - 25 nm. The flocced cloudberry-like aggregates of particles should have an average diametral size of less than 500 nm, advantageously less than 100 nm. If the pigment particles are applied in dry form, the solids of the applied coating should preferably be greater than 80 %.

In FI Pat. Appl. No. 973775 is disclosed a method of forming a paper or board web or any other web of basically fibrous structure, in which method a moving web-formation substrate is covered with a raw material furnish comprising cellulosic pulp fiber, plant fiber or other materials suitable for making a paper, board or nonwoven product. The raw material furnish fed onto the web-formation substrate is passed into at least one compression nip for forming a firm web from the laid fibers of the raw material. Next, the web-formation substrate is connected to a first electrical potential and a second potential higher than said first potential is applied displaced from said first potential at a distance above that side of the web-formation substrate on which the raw material furnish is being fed, whereby an electric field is established between said potentials. The voltage between said first potential and said second potential is adjusted so high as to establish a corona discharge in the vicinity of said higher potential, said discharge being capable of causing an ion blast from said higher potential to said lower potential, whereby said ion blast transports the particulate raw material exist-

ing in the space between said potentials onto said web-formation substrate and assures the adherence of the raw material to the substrate. In conjunction with the above-described method, the particles of web treatment material 5 can be fed in the web-formation step into the flow of the raw material fibers or, alternatively, directly onto the formed web in a manner described above.

In addition to a conducting wire or replacing the same, 10 the counter electrode of the ion-blast apparatus may comprise a conducting belt, possibly a plurality of belts, and in special cases, a roll or set of rolls, provided that such an arrangement can offer a sufficiently long distance of web travel for applying the raw 15 material. Also a construction with a nonconducting wire may be contemplated having at least one counter electrode placed under such a wire.

A product made according to the invention is characterized by having microscopic particles of the above-described mineral origin, advantageously small calcium 20 carbonate particles, applied on its surface and/or in its interfiber spaces.